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MASS-SPECTROMETRIC STUDIES OF GRAPHITE VAPORIZATION AT HIGH TEMPERATURES

Thomas A. Milne
Frank T. Greene
Stephen L. Bennett
Midwest Research Institute

TECHNICAL REPORT AFML-TR-70-192

February 1971

Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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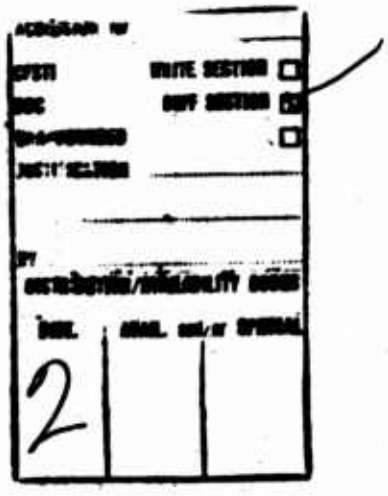

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FOREWORD

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under USAF Contract No. F33615-68-C-1709. The contract was initiated under Project No. 7360, "Chemical, Physical, and Thermodynamic Properties of Aircraft, Missile, and Spacecraft Materials," Task No. 736001, "Thermal and Chemical Behavior of Advanced Weapon System Materials." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. Paul W. Dimiduk (AFML/LPT) as Technical Monitor.

This report covers work conducted from 1 July 1969 to 30 June 1970. It was released by the authors in July 1970.

The work at Midwest Research Institute, designated as Project 3228-C, was performed by Dr. Stephen Bennett and Dr. Thomas A. Milne. Dr. Milne served as project leader; Mr. Gordon Gross provided technical management and Dr. Frank T. Greene participated in scientific discussions. Professor Paul W. Gilles, University of Kansas Chemistry Department, served as consultant.

This technical report has been reviewed and is approved.

HYMAN MARCUS, Chief
Thermo & Chemical Physics Branch
Materials Physics Division
Air Force Materials Laboratory

ABSTRACT

The progress in a second year of study of the thermodynamics of carbon vapor is reviewed. The status and preliminary performance of a high capacity, three-stage, high pressure sampling system--Nuclide HT-12-90 mass spectrometer detector and data acquisition system (including time-of-flight velocity analysis of beam neutrals) is presented. Beam system calibrations with Ar, N_2 and Ag indicate partial pressures of about 1×10^{-10} to 1×10^{-8} atm. (depending on background) can be detected from a Knudsen cell with a 0.040 dia. orifice placed 56 cm. from the ion source. A troublesome feature of the present ion source is that some modulation of background peaks occur in the presence of modulated beams. A series of attempts to heat graphite in vacuum to temperatures greater than 3000°K are described. Best results are obtained with slotted pyrolytic graphite cells but arcing still limits heating to 3000° to 3100°K. Carbon species through C_7 have been observed from a pyrolytic graphite Knudsen cell. The C_1 to C_5 data agree well with literature values, at the two temperatures of 2800°K and 2630°K. A correlation of dimer formation versus expansion conditions for a number of gases, studied to date, indicates that nucleation cannot be ruled out in high-pressure Knudsen cells or laser heatings.

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I.

INTRODUCTION

The ultimate goal of these studies is to extend our knowledge of the evaporation behavior of graphite to the 1 to 10 atm. total pressure regime. Considering that previous equilibrium or steady-state vaporization work (excluding laser or flash vaporization) has been limited to about 3200°K or less, representing a total pressure of less than about 10^{-3} atm., it can be seen that composition studies extended even 400°K to 3600°K (approaching 10^{-1} atm. pressure) would be a quite valuable addition to our knowledge of higher molecular weight carbon species behavior. Furthermore, since at these pressures perturbation of the sampled composition may occur due to continuum sampling effects, studies over the range 3000°K to 3600°K should be an especially valuable beginning in the ultimate characterization of vapor composition at the boiling or triple point. Because free evaporation is expected to be so ill-defined at higher temperatures, with a heterogeneous solid phase like graphite and with the advent of gas collisions during evaporation, we have chosen to concentrate primarily on equilibrium studies.

The work accomplished during the first year of this project is best summarized by repeating the abstract from Technical Report AFML-TR-69-225 (Ref. 1):

"In connection with our goal to extend the thermodynamics and kinetics of carbon vaporization toward the 1 atm. regime, we review, briefly, related work currently under way in several laboratories. Our own first year's research is then described in terms of prospective sources of carbon vapor, the problems of cold-probe sampling of hot gases and the important continuum sampling effects of mass separation and nucleation. Studies of cold-probe, hot gas interaction were carried out using the Bendix TOF direct sampling system. With flames at about 2500°K time-of-flight velocity analysis indicated the possibility of serious cooling by heat exchange to the cold orifice. Better controlled experiments at 1000°K, using rare gases heated in a furnace flow system, gave no definite indication that sampling was not adiabatic. Considerations of free-jet expansion behavior serve to allow estimates of the conditions of carbon vaporization at which continuum effects may become important. Continuum effects could be quite significant in laser evaporation and in free evaporation from large surfaces (~ 1 in.) above 3000°K. A new, high pumping speed, 3-stage, differentially pumped, modulated beam, direct sampling system is described. Beams are detected by a Nuclide mass

spectrometer with several data acquisition options. The work planned for the second year emphasizes techniques of fast data acquisition and continuum sampling effects with carbon vapor."

In this report are presented the research results of our second year of effort, devoted primarily toward achieving mass spectrometric analysis of the effusate from graphite Knudsen cells at temperatures beyond 3000°K.

II.

BRIEF REVIEW OF RECENT CARBON VAPORIZATION STUDIES

As was done in the first annual report, but more briefly here, we summarize highlights of recent work in other groups that is of particular relevance to our carbon vaporization studies.

Steele (Ref. 2), has reported preliminary equilibrium heats of vaporization for C_2, C_3, and C_4 relative to C_1. The measurements extend to about 3100°K in the case of C_4 and are in good agreement with the lower temperature Knudsen cell work of Drowart et al. (Ref. 3), which extended to only 2700°K. Free evaporation measurements on C_4, C_5, and C_6 are also reported at temperatures to 3150°K. Appearance potential curves for C_3^+ show excessive tailing near threshold, possibly due to fragmentation from higher clusters or to low lying excited states of C_3. Pulsed heating experiments give evidence also that C_3^+ is not pure parent ion at very high temperatures.

Zavitsanos (Ref. 4), reports equilibrium composition studies for pyrolytic graphite (PG) contained in small PG or tantalum carbide Knudsen cells. A tantalum shield was placed over the PG lid containing the tapered orifice hole to prevent surface-evaporated carbon from reaching the mass spectrometer, hopefully by completely scavenging all vapor not passing directly through the hole in the tantalum shield from the orifice. The PG crucible studies covered the range 2493°K to 2929°K while the tantalum carbide crucible was heated to 3003°K. Glowing and arcing was reported to have made measurements difficult at temperatures above 3000°K. Second-law heats of vaporization for C_2 and C_3 were larger than Drowart et al. (Ref. 3). Only a third-law heat was obtained for C_4, due to its observation only at the highest temperature.

Waachi and Gilmartin (Ref. 5), report in detail on their extensive measurements of the free evaporation behavior of a variety of graphites using resistance heated filaments and mass spectrometry. PG was studied at temperatures to 3260°K. The variety of behavior and phenomena reported establish that "free evaporation" of graphite is not a well defined process.

Williams (Ref. 6), has completed electron impact studies of the appearance potentials of C_1, C_2, and C_3 and the fragmentation of C_3 to C_2^+ from which he deduces a heat of formation of C_3 at high temperatures.

Crawford (MIT) and Hoch (University of Cincinnati), continue work on the ionization cross sections of carbon species and evaporation-condensation coefficients, respectively, but no new published information is currently available to us.

Altman (NASA-Ames) is treating the partition function for C_3 in terms of a limited number of bending vibrational states. Lincoln (NASA-Ames) is preparing for continued laser-graphite interaction studies.

Clark and Fox (Ref. 7), have carried out an interesting series of experiments involving the rate of vaporization of graphite filaments which are pulse heated in vacuum and helium. Temperatures of 3400°K were reached and total rates of vaporization were measured, although no mass spectral identification of vapor species was made. From first, second, and third law analyses of the total rate of vaporization and heat input to the filaments, the surprising conclusion was reached that C_2 is the dominant vaporizing species above 3000°K. Although the results appear consistent with the C_2 assumption, the evidence does not appear strong enough to rule out an appropriate mixture of C_1, C_2, and C_3 as an alternative explanation. Two of their observations are pertinent to our planned work. First, the phenomena of soot formation from evaporated carbon (Ref. 8) obscuring optical temperature measurements was observed in He or Ar at about 3200°K and in vacuum at about 3400°K. Second, as temperatures approached 3420°K in vacuum, the filaments had a tendency to arc, with the carbon vapor phase presumably carrying a significant amount of the current. The presence of He or H_2 suppressed arcing and allowed higher temperatures to be used. Since low voltages were used for these resistance heating experiments, this arcing is somewhat ominous in terms of our relatively high voltage RF heating approach.

III.

RESEARCH RESULTS

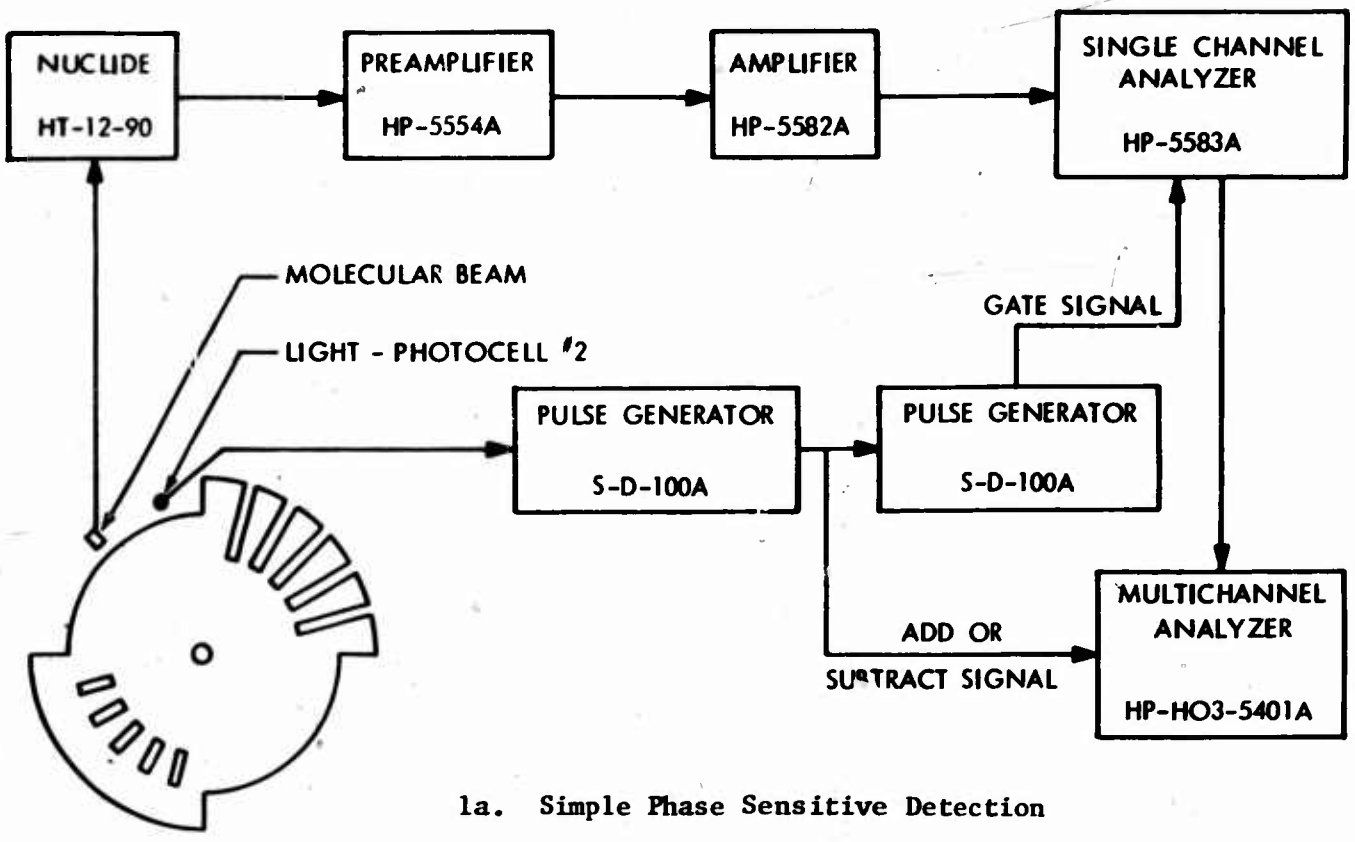
The development and present status of the four principal categories of equipment are first summarized followed by the results of preliminary performance tests of this equipment. Next is discussed the all-carbon Knudsen cell design which offers hope of achieving temperatures beyond 3000°K. Finally some thoughts about the likely importance of continnuum effects are presented in the form of a correlation of dimer formation in free-jet expansion of several gases (none of which remotely resemble carbon vapor).

A. Status of Equipment

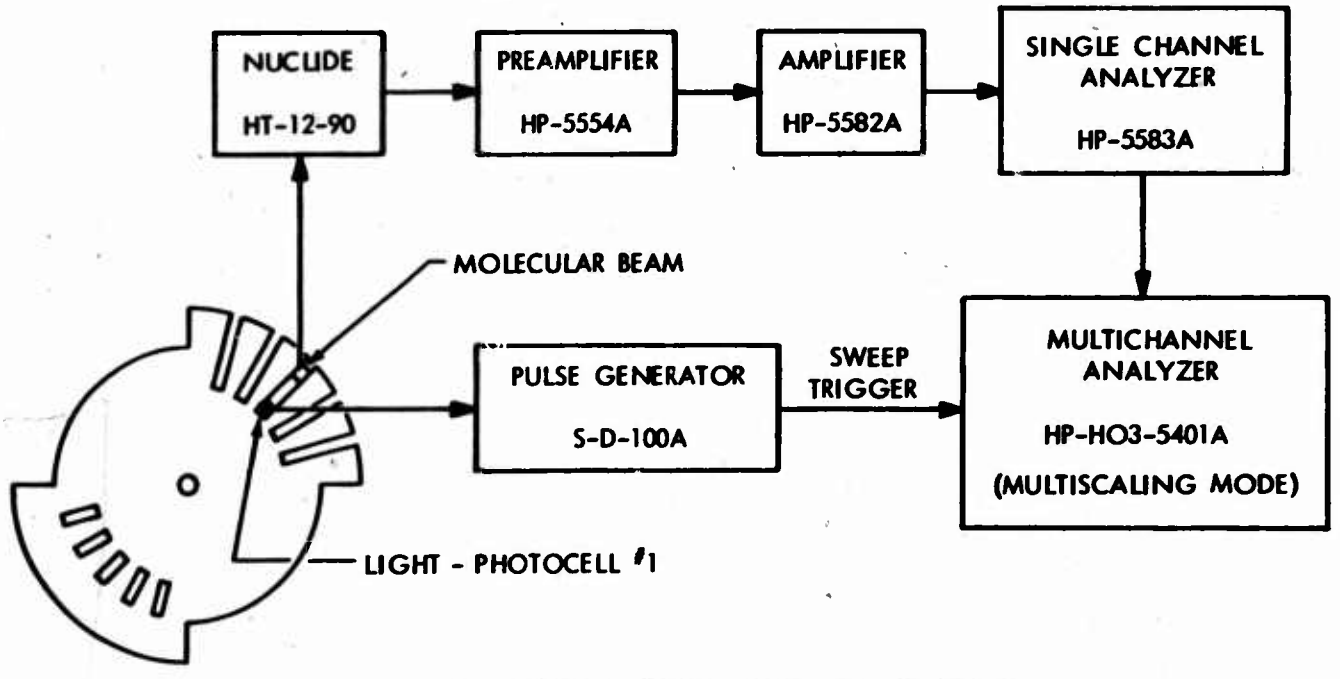
1. Beam-sampling system. The high capacity, direct, molecular beam sampling system described in Ref. 1 was completed and tested with permanent-gas beams early in this reporting period. The system operates continuously with DC-704 oil in the National Research Corporation 16 in. pump (Stage 1) and Santovac-6 in the National Research Corporation 6 in. pump (Stage 2). Refrigerated baffles operate at about -60°C and the pumps are supplied with water-cooled cold caps. No liquid nitrogen is required for the entire system. An Ultek rare-gas ion-pumped third stage separates the oil-pumped regions from the mass spectrometer. There is as yet no evidence of oil contamination from these trapped lower stages.

2. Time-of-flight measurements - data acquisition. The final components (see Appendix) have been received for the application of phase sensitive detection and time-of-flight velocity analysis using direct ion counting. Figures 1a and 1b show the components chosen and the block diagram for the two principal modes of operation anticipated in the carbon program. In Figure 1a, the setup for simple chopping and phase-sensitive detection is indicated. In Figure 1b is shown the arrangement of chopper and electronics for time-of-flight velocity measurements during steady-state evaporation experiments.

The function of the multigrooved chopping disk has been described in Ref. 1. For simple, phase-sensitive detection and for finding the beam prior to the time-of-flight measurements, the second photocell and two wide slots are used, along with pulse shaping that permits a gate-open signal to be produced only by the wide slots. A single channel of the multichannel analyzer will be used as a reversible counter via the sense switch provided. This system is patterned after that developed and tested by Greene and described in Ref. 9. For time-of-flight measurements, the first photocell, which is positioned to respond only to the same narrow slot by which the beam is chopped, triggers the multichannel analyzer to



1a. Simple Phase Sensitive Detection



1b. Time-of-Flight Velocity Analysis

Figure 1 - Block Diagrams of the Two Modes of Data Acquisition Using Beam Chopping, Ion-Counting and the Multichannel Analyzer

start a sweep in the multi-scaling mode. This sweep is repeated for each beam pulse and is followed by an equal number of equivalent cycles with the beam off and the analyzer in the subtract mode if it is desired to subtract off background.

For the initial beam tests described in this report, a simple two-slot, chopper disk was used. Driving the motor at 50 cps produces a 100 cps chopped beam signal. This signal is amplified by the standard HT-90 electrometer (with an internal capacitor removed to improve time response) using a 10^9 Ω input resistor. The output of the electrometer, which appears on an oscilloscope as a well defined square wave, is fed to a Princeton Applied Research phase locked amplifier, Model JB-4 or equivalent.

3. Mass spectrometer. The Nuclide HT-90 single focussing, magnetic mass spectrometer was delivered just prior to this reporting period. Upon installation it appeared to meet specifications and was accepted, although a high voltage arcing problem in the ion source remained to be corrected. Several electronic malfunctions, involving chassis and cables, were corrected and the machine was thought to be operating satisfactorily when the permanent gas beam tests mentioned above were begun. This assessment proved to be premature. During the testing of the new beam system with argon clusters, several serious problems appeared intermittently. The principal one was a variability in apparent multiplier gain with signal strength. This problem, which manifested itself as a decrease in gain with weaker signals, was finally diagnosed as a floating dynode near the end of the multiplier dynode string. With appropriate rewiring within the multiplier housing, the problem was corrected.

Three other potentially more serious problems, as yet uncorrected, are discussed below under the section on preliminary system performance. With the exception of these problems and with the possible addition of a fast, peak-switching device, the mass spectrometer system is complete and operational.

4. RF induction furnace. The 30 kw., 450 kc. RF generator has been installed and operates satisfactorily. Its use is anticipated for all carbon heating in the present program, possibly with the use of a stepdown transformer. Laser surface-heating studies, originally considered, are not presently contemplated in view of their ambiguity in yielding equilibrium data. The kind of work coils and susceptors used are discussed in a later section.

B. Preliminary System Performance

1. Beam behavior - permanent gases and silver. The first combined tests of the sampling system and mass spectrometer employed argon at 1 to 5 atm. in a conventional supersonic beam. Argon was chosen because of our extensive experience with it in connection with our Bendix TOF - sampling system used for past work and for the early cold-orifice observations.

Typically, with a beam formed from 5 atm. of argon at room temperature, expanding through a 0.004 in. dia. orifice, the pressures indicated in Table I are obtained by ion gauge or ion-pump readout:

TABLE I

TYPICAL OPERATING PRESSURES IN MOLECULAR BEAM - MASS SPECTROMETER COMBINATIONS

Stage 0	5 atm.
Stage 1	1.3 μ
Stage 2	2.5×10^{-5} torr
Stage 3	8×10^{-7} torr
Beam swallowing	3×10^{-7} torr
Ion source	5×10^{-8} torr
Analyzer region	2×10^{-8} torr

Under these conditions, a very well collimated and almost completely swallowed beam is formed. Ordinary shutter effects, either by imposing the Nuclide shutter plate or the chopper disk, are typically 95% for argon monomer. The ratio of $80^+/40^+$ from a partly nucleated argon beam is found to be constant at all chopping frequencies from 0 to 260 cps. This is a sensitive test for the presence of a significant contribution to an observed beam signal from the scattering of the beam in the ion source. Thus, for an incompletely swallowed beam of argon monomer and dimer, the shutterable 40^+ signal (assuming no significant contributions from Ar_2) will arise from (1) the Ar on its first pass through as a beam, (2) the part, if any, of the Ar beam reflected directly through the electron beam, (3) the Ar beam after scattering in the ion source and at the steady-state pressure determined by the rate of pumpout, and (4) the scattered Ar_2 beam, converted to scattered Ar. The shutterable 80^+ signal, on the other hand, in view of the extreme instability of the Ar_2 molecule, will consist only of contributions from the Ar_2 molecules on their first pass through the ion source. The general effect is that slow chopping, or shuttering, can lead to an overestimate of noncondensible components of a beam relative to condensible or unstable beam components (Ref. 10). Without the beam swallowing feature

of our beam system-mass spectrometer, this effect is noted with the HT-12-90 ion source. When the beam swallowing pump is turned off, the shutterable 40^+ signal increases by about 12% while the shutterable 80^+ remains constant. The 100 cps chopped signals are unaffected.

With the large pumping speeds provided, we found it possible to work with rather large skimmer diameters (up to 3/16 in. dia. holes in the apex of 60-degree cones have been used) without appreciable sacrifice in beam intensity. The use of such large skimmers could be important in studies with condensible components in permanent gases. For argon, beam intensity was relatively sensitive to orifice-to-skimmer distance, peaking over a range of about 5/8 in. to 2-5/8 in. of separation at about 1-5/8 in. (400 orifice dia. downstream for a 0.004 in. orifice, or well beyond the transition to collisionless flow). The system has not been operated at higher source pressures but is expected to work well at, say, 500 atm. with a 0.001 in. dia. orifice.

A series of argon cluster intensities were determined for 5 atm. of argon expanding through a 0.004 in. orifice. Table II shows a comparison of results with those previously established with the Bendix mass spectrometer. These preliminary results are in qualitative agreement with the much earlier Bendix results (Ref. 11). Part of the discrepancy is caused by the usual circumstance that focusing conditions must be continually changed for optimum ion collection. Table II data were obtained from a scan focused on 80^+.

TABLE II

A COMPARISON OF CLUSTER-ION INTENSITIES FROM THE POSITIVE-ION MASS SPECTRA OF A HIGH PRESSURE BEAM FORMED BY EXPANSION OF ROOM TEMPERATURE ARGON THROUGH A 0.004 IN. DIAMETER ORIFICE

		Relative Intensity	
Condition	Ion	Bendix TOF	Nuclide HT-12-90
5 atm.	40^+	100.0	100.0
	80^+	21.0	5.5
	120^+	7.0	2.7
	400^+	0.9	0.26
	760^+	0.27	0.107
	800^+	0.15	0.062
	840^+	0.29	0.112
	1000^+	0.13	0.064

In a scan of argon clusters extending out to mass 4040 (Ar_{101}^+), it became impossible to optimize ion focusing conditions for the higher mass ions, presumably due to their large momentum at right angles to the ion beam direction. Minor changes in the ion source should allow focusing of these heavier ions. Nevertheless, such heavy ions could be readily detected. Figure 2 shows selected portions of this scan. Note the increased importance of the $Ar_{n-1}^{40}Ar^{36}$ peak as mass increases. Metastable argon cluster peaks were observed as well. Their study could be revealing in term of better understanding of cluster fragmentation behavior.

Intensity measurements with 1 atm. Ar and N_2 beams were used to establish beam detection sensitivities for the Nuclide under various conditions of interest to carbon studies. Multiplier signals of 2×10^{-8} amps were obtained from a 1 atm. beam of argon through a 0.004 in. dia. orifice at a distance of 56 cm. from the ion source electron beam and at 50 ev electron energy, 1 ma. emission current and a minimum multiplier gain of about 500. At full multiplier gain, about 10^6, noise measurements between peaks 35 and 36 indicate that in the absence of background contamination, species in a 1-atm. beam at a partial pressure of about 3×10^{-7} atm. can be detected without phase-sensitive detection and with a signal-to-noise ratio of 1 and a time constant of a few seconds. The noise under these conditions appears to be dominated by that from the multiplier. With phase-sensitive detection and available integration, such levels can be detected in the presence of appreciable background contamination at masses of interest. For example, the present background at mass 36^+, which is rather high and variable in our system, would appear to limit 36^+ beam measurements (for a signal-to-noise ratio of 1) to partial pressures of about 2×10^{-6} atm. for a 0.004 in. source 56 cm. away when strip chart recorder output is used with a 10 sec. time constant on the phase-locked amplifier output. With a graphite, free-evaporation source of 0.040 in. dia. yielding about 100 times more intensity, we estimate that C_3 can be detected at surface temperatures of about 2400°K, allowing for the evaporation coefficient of C_3. The use of pulse counting techniques is expected to permit extension of the detectability, as is lowering of the rather large 36^+ background by pump and system bakeout. In similar experiments with N_2 beams it was determined that the detectability of 36^+ above background, at 17 ev, was still about 2×10^{-6} atm. for the 0.004 in. source. Table III shows typical signal and noise levels (1/2 of peak-to-peak noise variation and zero).

To confirm this sensitivity we heated silver in a large, open graphite crucible where the expected effective evaporation area, governed by skimmer and other beam system orifice diameters, was about 0.080 in. dia. This rough calibration again indicated species detectability of about 1×10^{-6} atm. at 36^+, consistent with the argon and N_2 calibrations. During the silver calibration runs, qualitative agreement with literature heats of evaporation and ratios of monomer-to-dimer (Ref. 12) was obtained.

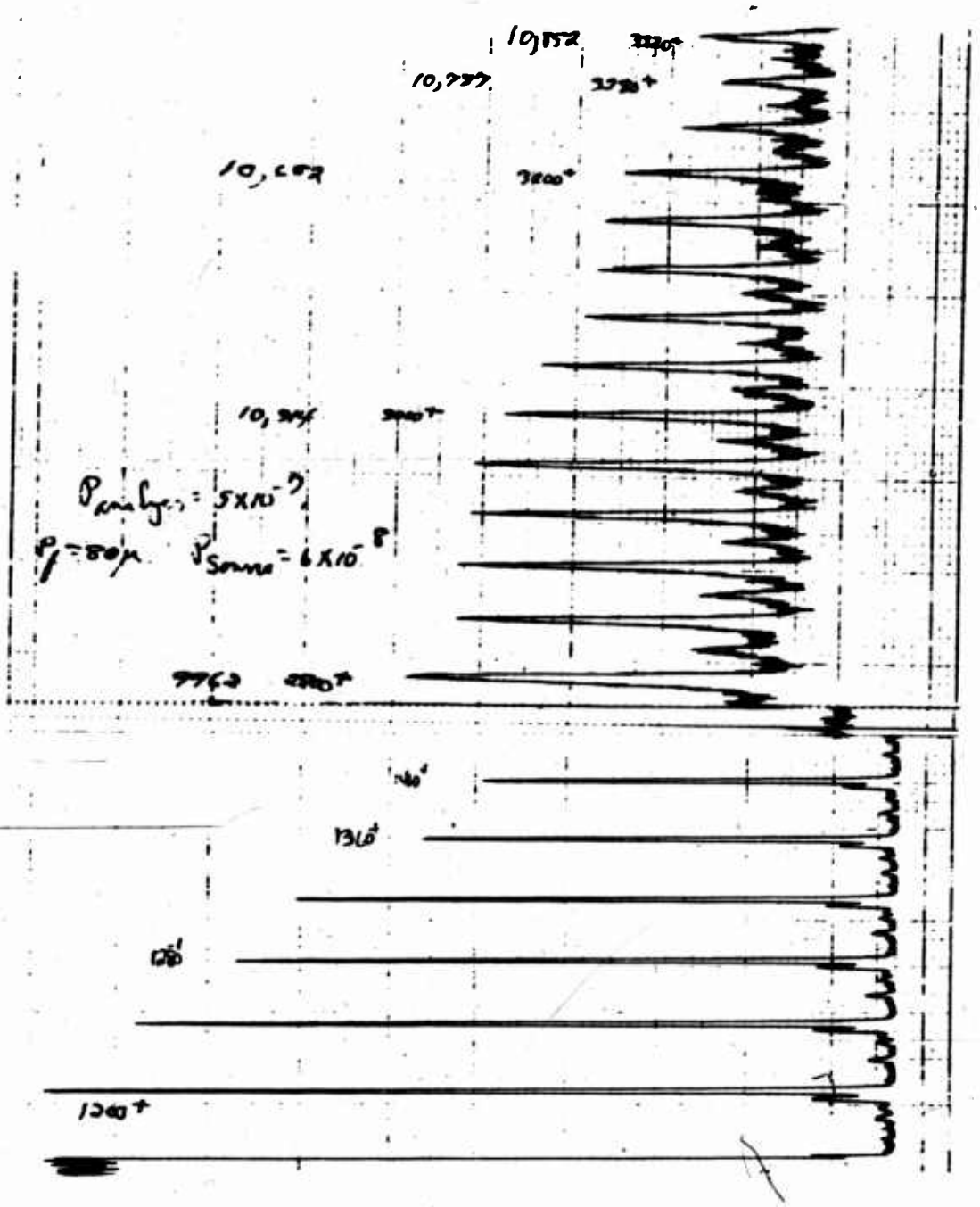


Figure 2 - Direct Reproduction of Strip Chart Recording of Scan of Argon Clusters at Very High Masses. Molecular beam formed from expansion of 5 atm., 300°K argon through a 0.004 in. dia. orifice. Electron energy 50 ev.

TABLE III

TYPICAL BEAM COMPONENT AND BACKGROUND NOISE INTENSITY LEVELS FOR PHASE-SENSITIVE DETECTION OF A 1 ATM. BEAM OF N_2 FORMED AT ROOM TEMPERATURE BY EXPANSION THROUGH A 0.004 IN. DIA. ORIFICE PLACED 56 CM. FROM THE ION SOURCE ELECTRON BEAM 17 EV ELECTRON ENERGY

	Mass Observed	Phase-Locked Signal Strength	1/2 Peak-to-Peak Noise with 10 Sec. Time Constant
1 atm. N_2 beam	28^+	6×10^8	
	29^+	4×10^6	
Beam shuttered off	36^+	0	$\pm 10^3$
	48^+	0	± 200
	Between peaks	0	± 10

2. Nuclide HT-90 behavior and problems. As we resolved the various electronic problems to be expected with any new system and proceeded to use the mass spectrometer routinely on both this program and a program of water studies for OSW (Ref. 13), three potentially serious remaining problems became apparent. These are: (a) the erratic presence of intense ion signals at 19^+ and 35^+; (b) the existence of a large 60 cycle modulation of all ion signals coming from the mass spectrometer, and (c) the modulation of all background peaks in the presence of modulated molecular beams.

a. The first problem has received little attention since it is not expected to interfere with the carbon work. The 19^+ and 35^+ peaks show very little dependence on repeller voltage and have a very high apparent appearance potential. These peaks are suspected of being surface generated ions resulting from the poorly collimated electron beam in the ion source supplied with our machine. (See ion source schematic in Figure 3.)

b. Identification of the source of the 60 cycle modulation on all peaks, which has been as large as 50% of the total ion signal at a given mass, has so far defied the efforts of MRI and Nuclide technicians. In normal electrometer-strip chart recorder measurements this modulation might be averaged out. For fast mass scans, of which our magnet is capable,

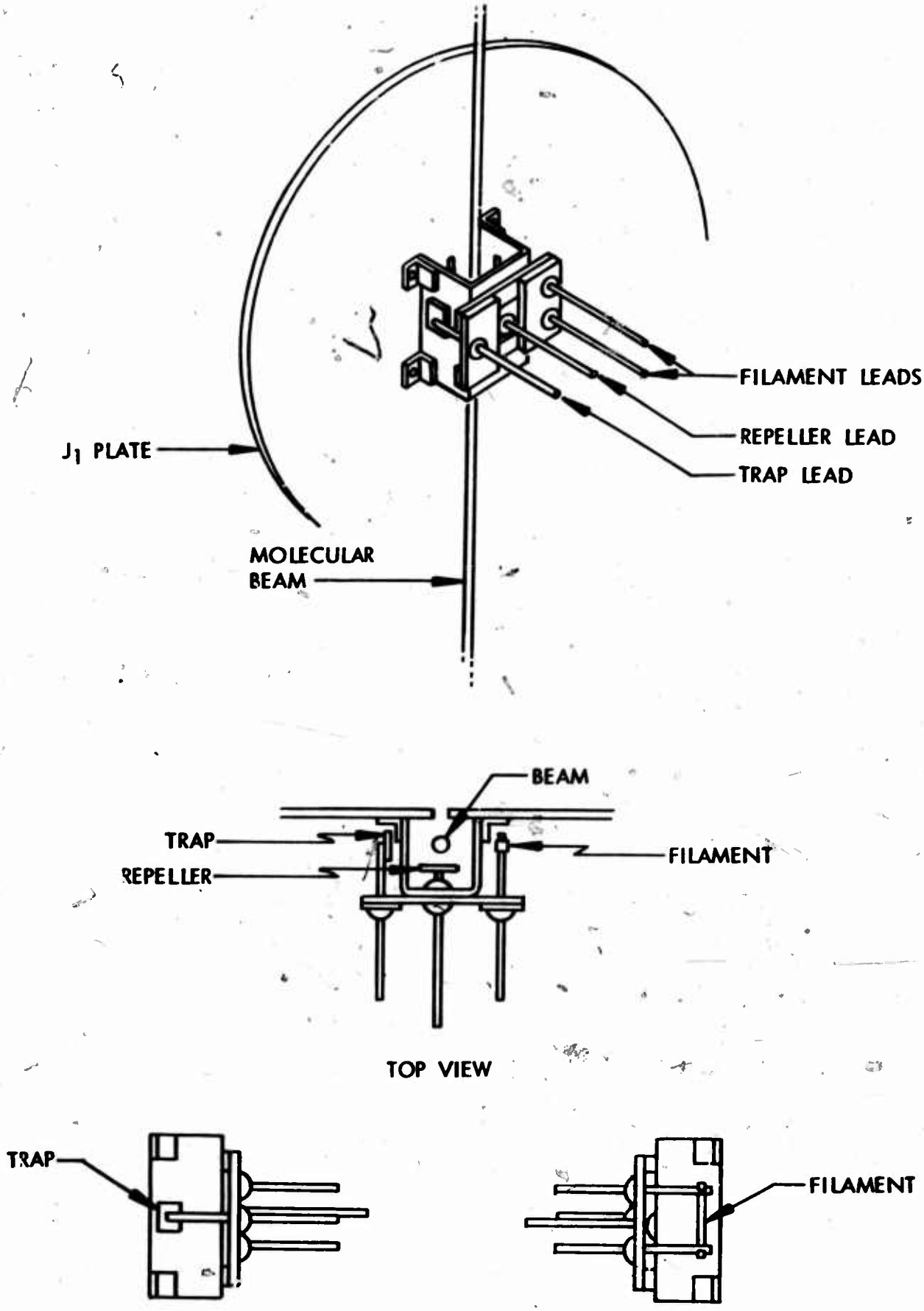


Figure 3 - Schematic of the Nuclide HT-12-90 Ion Source, Used in the Experiments Reported to Date

TABLE III

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	48^+	0	± 200
	Between peaks	0	± 10

2. Nuclide HT-90 behavior and problems. As we resolved the various electronic problems to be expected with any new system and proceeded to use the mass spectrometer routinely on both this program and a program of water studies for OSW (Ref. 13), three potentially serious remaining problems became apparent. These are: (a) the erratic presence of intense ion signals at 19^+ and 35^+; (b) the existence of a large 60 cycle modulation of all ion signals coming from the mass spectrometer, and (c) the modulation of all background peaks in the presence of modulated molecular beams.

a. The first problem has received little attention since it is not expected to interfere with the carbon work. The 19^+ and 35^+ peaks show very little dependence on repeller voltage and have a very high apparent appearance potential. These peaks are suspected of being surface generated ions resulting from the poorly collimated electron beam in the ion source supplied with our machine. (See ion source schematic in Figure 3.)

b. Identification of the source of the 60 cycle modulation on all peaks, which has been as large as 50% of the total ion signal at a given mass, has so far defied the efforts of MRI and Nuclide technicians. In normal electrometer-strip chart recorder measurements this modulation might be averaged out. For fast mass scans, of which our magnet is capable,

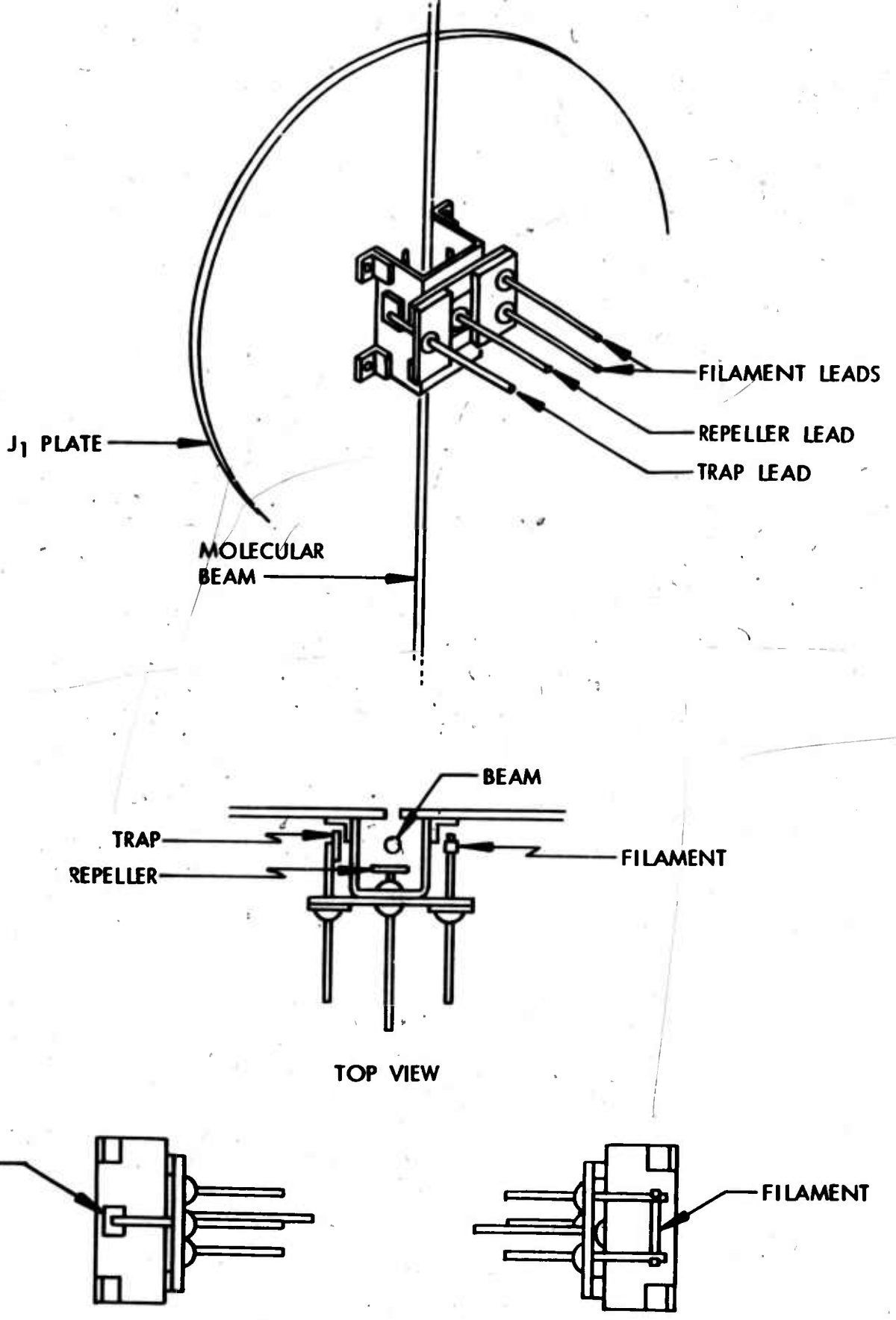

Figure 3 - Schematic of the Nuclide HT-12-90 Ion Source, Used in the Experiments Reported to Date

or for fast data acquisition via the multichannel analyzer in time-of-flight velocity experiments, this 60 cycle modulation could seriously perturb results of single sweeps or degrade signal-averaging in multiple sweeps.*

c. The third problem is potentially the most serious for modulated beam detection of minor species in strong beams. In preliminary studies with intense argon beams, prior to actual vaporization experiments, it was observed that at beam chopping frequencies of 100 cps all background peaks were appreciably modulated in-phase with the true beam peak. The modulation percentage of the background was approximately constant for all background peaks tested, ranging from He^+ to Hg^+, with the exception of 19^+ and 35^+ peaks which were significantly less modulated. Under some conditions the effect was not readily detectable in the DC level of the background peaks while under others it was and was reflected in spurious shutter effects for ion-source background species.

Several diagnostic tests were performed to establish the cause of the background modulation effect. Gas was leaked into Stage 2 of the sampling system, to pressures far greater than any background gas component, and it was observed that no enhancement in the percentage of the background modulation was caused. Furthermore, background gas coming mainly from the ion source was modulated to the same extent as background gas coming mainly from the sampling system, also arguing against a molecular beam knock-on or other effect in the sampling system region. When the argon beam was misaligned by moving the orifice laterally, the background modulation decreased monatonically with beam strength. The background modulation was not affected by the source slit width but was slightly affected by emission current and J_2, the extraction voltage on the first ion accelerating grid. The higher the emission current, the larger was the percentage of the background modulation, while the higher the potential on J_2, the lower was the modulation effect.

By far the most important variable in altering the extent of background modulation was the repeller voltage, which in effect pushes the ions out of the ion source, and therefore largely determines their residence time in the ion source. The effect of this parameter on AC and DC signals for a 100% beam signal (Ar_2^+) and for a large background peak (28^+) is shown in Figures 4 and 5. (The main beam signal, 40^+, showed very similar behavior to the 80^+ signal.)

In Figure 4, the Ar_2^+ behavior is seen to be a complex function of repeller voltage (with all other ion-source parameters optimized at each repeller setting). The peak signal on AC or DC occurs at nearly zero repeller voltage. The large shoulder at negative repeller voltages occurs also for 40^+ and is not explained at present. The AC/DC ratio is quite constant, confirming that the 80^+ signal arises almost entirely from the direct molecular beam.

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* Nuclide personnel recently established that the 60 cycle modulation arose in the emission regulator circuit and suggested changes which eliminated the problem.

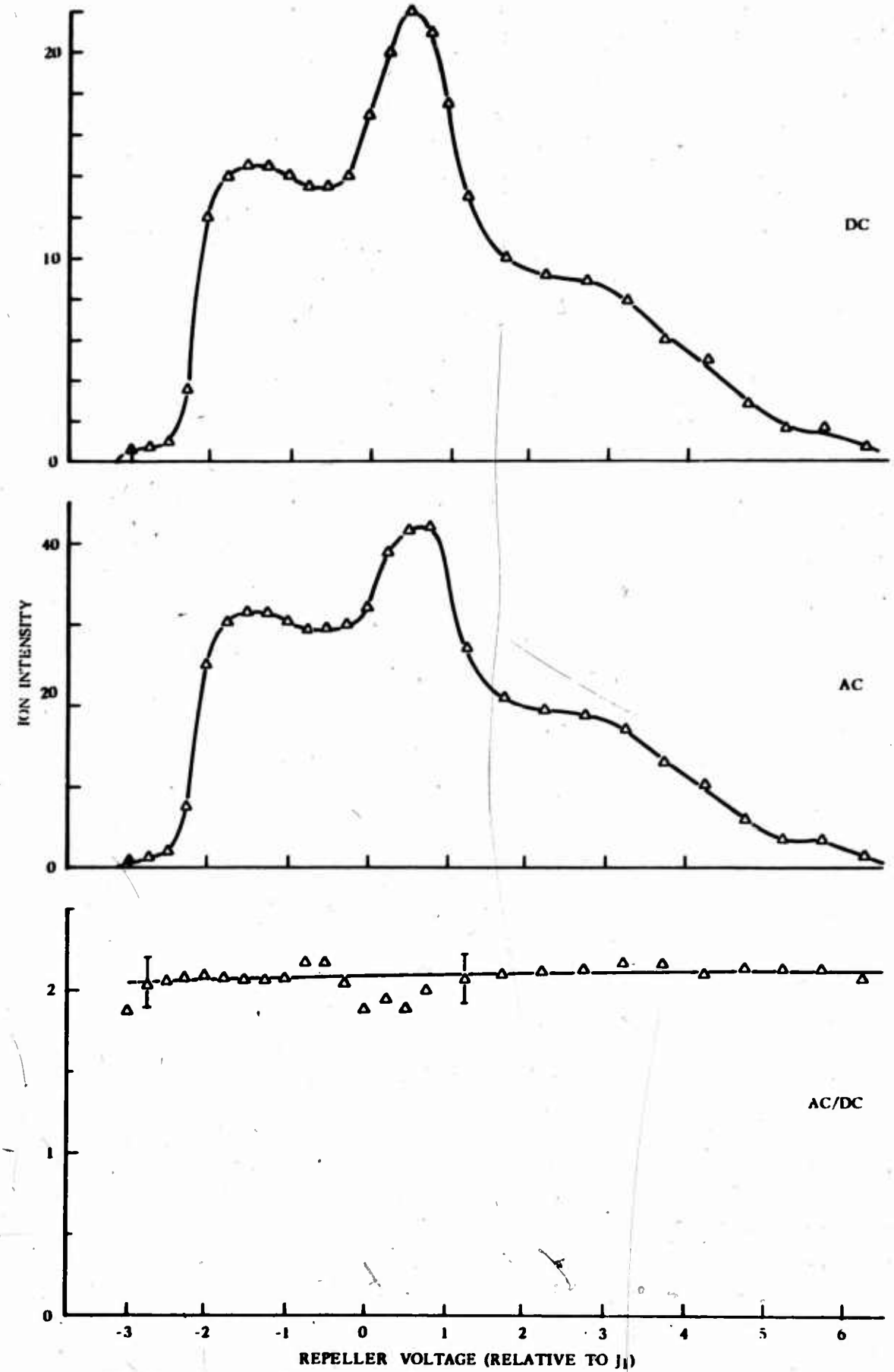

Figure 4 - The Effect of Ion Source Repeller Voltage on AC and DC Signals from Ar_2^+ Coming from a Well-Collimated, Almost 100% Ar_2 Component of a Modulated Supersonic Beam of Argon. Chopping speed 100 cps. Beam entering ion source approximately 0.1 in. dia.

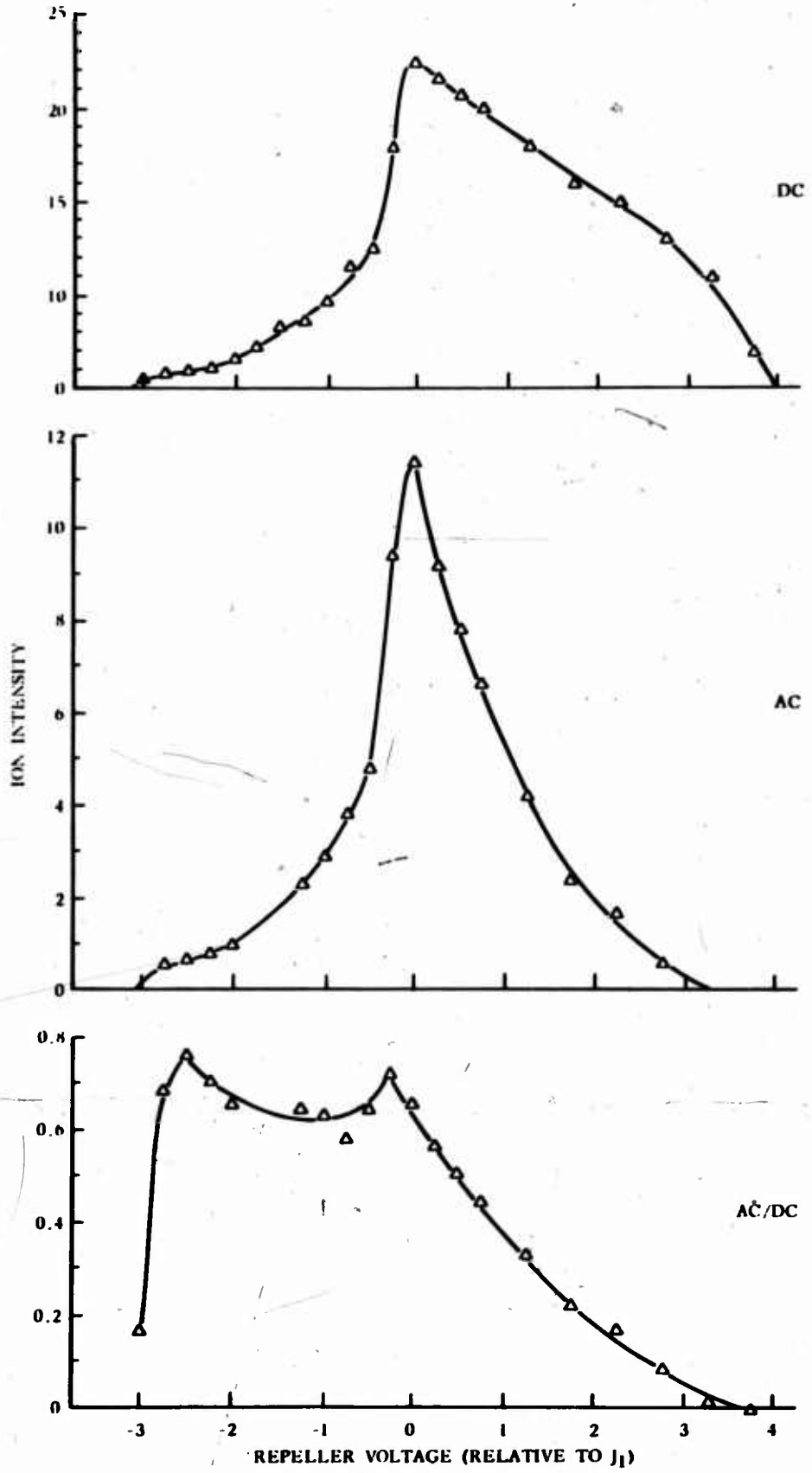

Figure 5 - The Effect of Ion Source Repeller Voltage on the AC and DC Signals for 28^+ Background Ions, in the Presence of a Strong, Modulated Argon Beam

Figure 5 shows similar data for a background peak in the presence of the strong Ar beam. Note that the shapes of the AC and DC signals are different for AC and DC and from the corresponding beam peaks in Figure 4. Most significant is the observation that at large repeller voltages the AC component of the background peak goes to zero. In fact, from the two graphs one can see that at one setting the 28^+ AC component was reduced by two orders of magnitude under repeller conditions such that the beam AC signal is reduced by only about a factor of 3 from its maximum value. Phase was not adjusted during these experiments.

Further experimentation with sets of ion source parameters showed that at certain repeller voltages, the background peaks could be modulated either in or out of phase with the main beam signal, depending on the J_2 setting. Furthermore, different background peaks showed slightly different behavior with J_2. It was also established that the phase shift of the phase-locked amplifier affected the relative magnitude of the AC background modulation and the AC beam signal. This phase delay depended on repeller voltage, as shown in Figure 6, and probably on other ion source variables not investigated. A phase shift between beam and background of some tens of degrees is indicated in Figure 6 at zero repeller voltage, indicating time lags in ion behavior in the ion source of the order of milliseconds.

In summary, although the many interlocking parameters were not systematically studied, the percentage of background modulation could be materially altered relative to the beam modulation signal by repeller voltage, J_2 voltage and phase delay in the phase-locked amplifier. Through compromise settings of these parameters to minimize background modulation, we were able to observe beam species from strong beams at the parts-per-million level with negligible background modulation of adjacent masses of comparable strength. As an example, the species $(Ar^{40}Ar^{38})^+$ from the mixed dimer in an argon free jet, with an estimated mole fraction in the beam of 6×10^{-6}, was readily detected as an AC signal in the presence of background peaks of comparable strength which were negligibly modulated. It thus appears that this effect can be made unimportant in carbon studies where beam intensities will usually be less than those from 1 atm. argon beams. When intense carbon beams are ultimately encountered, this effect can be adequately minimized as described. We speculate that the modulation is caused by the effect of the positive ions from the beam on the efficiency of escape of background ions from the ion source or on the alteration in electron beam space charge trapping of these ions.

In further studies of this phenomenon in connection with water vapor studies it was established that the background modulation was still important with effusive beams having an intensity at the ion source comparable to those encountered in many high-temperature investigations. Nuclide Corporation is cooperating with us in seeking ion source design changes to eliminate or minimize this effect.*

* Recent modifications of the ion source by another project have reduced the background modulation several orders of magnitude to below the limit of detectability.

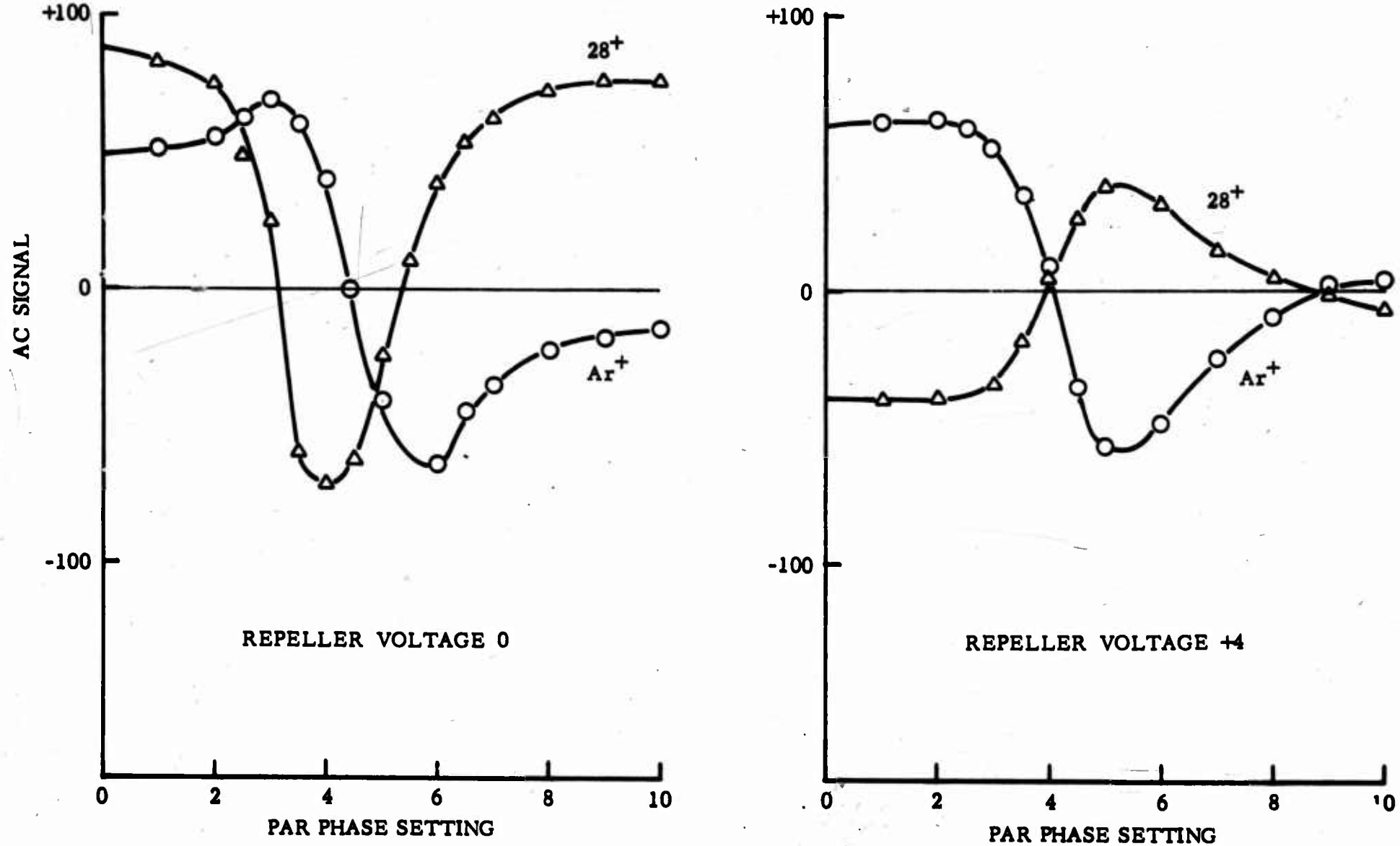

Figure 6 - Effect of Phase on Phase-Locked Signals From a Beam ($^{36}Ar^{+}$) and Background (28^{+}) Peak, at Two Different Repeller Voltages, in the Presence of a Strong Ar Beam. J_2 held constant for each repeller voltage. (0-10 PAR settings correspond to about 180 degrees.)

3. RF heating tests. The 30 kw., 450 kc. induction furnace (Westinghouse Type 50K64) has been installed and tested. With an unshielded coil in the vicinity of the mass spectrometer, noise pickup by the electrometer was disastrous. Consequently, our initial graphite heating arrangements have incorporated carefully shielded leads and coils. Such shielding has eliminated interference problems.

The attempts to achieve high temperatures in graphite specimens approximately 1 in. dia. x 1 in. high can be divided into four classes. Each of these will be described briefly.

a. The heating arrangement initially chosen for graphite vaporization involved the primary RF coil outside the vacuum system with a copper current concentrator placed just inside a 4-in. O.D. Pyrex pipe. The inside of the current concentrator was large enough to accommodate 1-in. dia. specimens. The system is illustrated in Figure 7. This arrangement was chosen to avoid having to introduce large RF currents through vacuum system walls and to optimize the heating of small specimens.

In initial heatings the system appeared to work satisfactorily, but as power was increased to achieve graphite temperatures approaching 2600°K, gaseous discharges often occurred. On one occasion the discharge apparently led to overheating of the concentrator and a portion of the copper melted. Several changes, involving flange cooling, shielding of the glass with ceramic and increasing the thickness of the concentrator walls, did not eliminate the occurrence of discharges. Likewise, it was noted that quite high Stage 1 pressures were created in spite of the large pumping speed provided by the 16-in. diffusion pump. The evidence to date points to the cause of the trouble as excessive outgassing of the ceramic, Pyrex walls and heated flange parts, coupled with quite restricted pumpout of the lower section of the concentrator compartment. Thus, pressures may be approaching a micron or more in the region where the discharge is seen to initiate.

During the course of testing and modifying this original graphite heating arrangement, four heatings of graphite were accompanied by mass spectrometer searches for a C_3 beam. These heatings ranged from about 2400°K to 2700°K apparent temperatures (through black body holes in the bottom of the graphite disks). The first heating was carried out before RF shielding was completed and interference with the AC detection was appreciable. The next two heatings, which also showed no 36^+ beams, were made under circumstances where the skimmer at some point overheated and fell, blocking line-of-sight for the graphite vapor. The best experiment, with shielding from noise, an intact skimmer and AC detection was plagued by discharges and Stage 1 pressure buildup so that a temperature of only about 2550°K could be safely achieved. No phase-locked 36^+ was seen, but

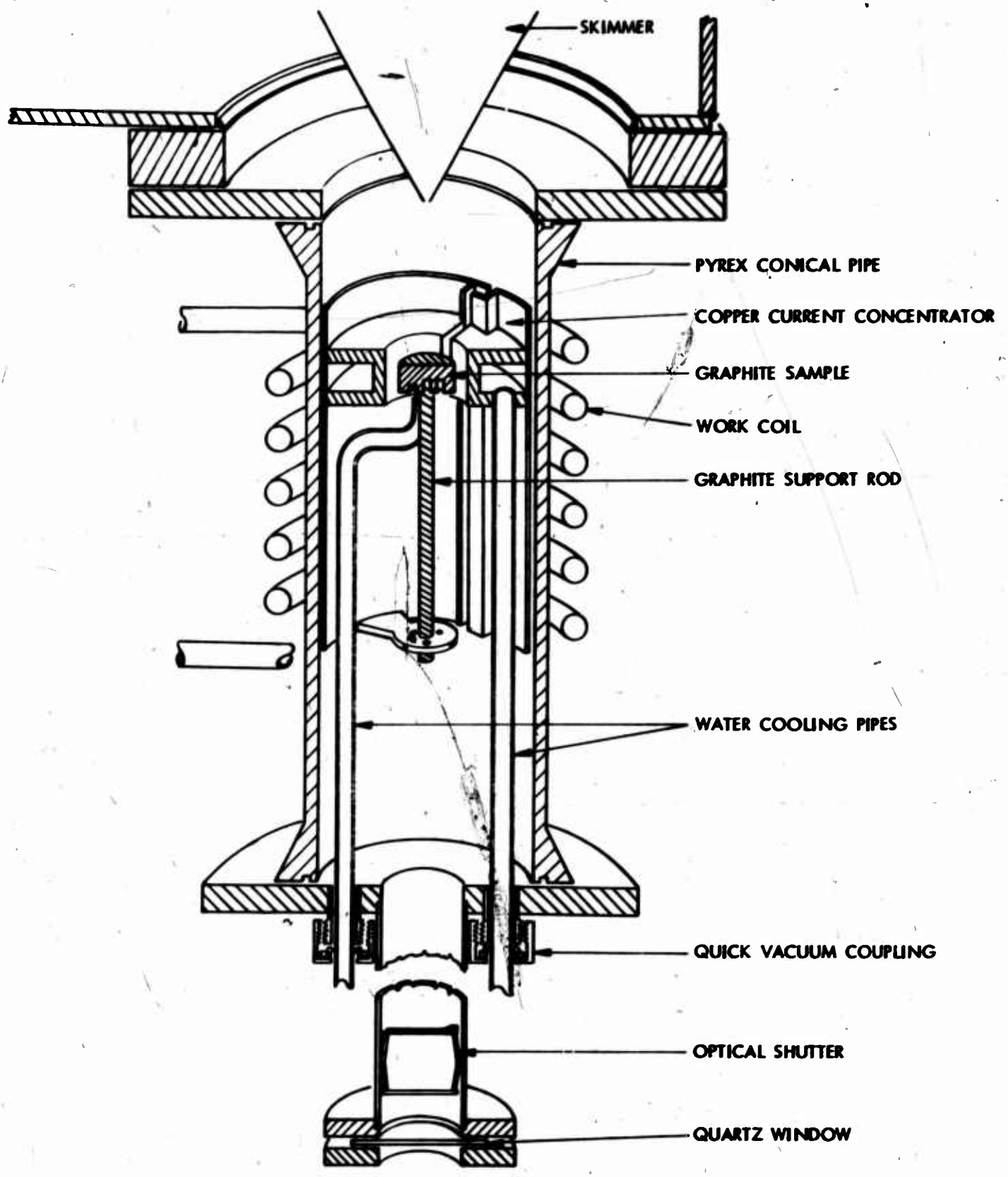

Figure 7 - Schematic of the Apparatus Used in Heating Graphite Cylinders to Temperatures Near 3000°K Using RF Heating and a Current Concentrator

the temperature was only marginally sufficient to expect positive results. It is also a possibility that extensive pressure buildup in the vicinity of the heated graphite, due to the outgassing problems mentioned above, was sufficient to scatter the graphite beam.

Also during these first vaporization studies we calibrated our seldom-used L&N optical pyrometer by comparison with a pyrometer recently calibrated by the Bureau of Standards for the University of Kansas. Our pyrometer was giving readings of from 50°C to 300°C high depending on scale. It was returned to L&N for repair and calibration. The temperatures quoted above are corrected temperatures based on the pyrometer comparison.

b. Since these problems occurred at well below the desired graphite temperatures, we next chose to introduce the RF coil into the vacuum system. The glass and ceramic shielding were eliminated and the large coil and the current concentrator were placed directly in a housing which consisted essentially of a 7-in. brass, water-cooled tee. A schematic of this system is shown in Figure 8, but with the later elimination of the current concentrator. Pumping speed in the vicinity of the graphite specimen was greatly increased but still restricted in the area immediately inside the concentrator ring. RF power entered through a Varian bakeable RF feedthrough, Model No. 954-5016.

The tests of this heating arrangement were carried out at the far end of our large sampling system, using the large Stage 1 pumping capacity, while Stages 2, 3 and the Nuclide were used for water-vapor, Knudsen studies for another project. Unshielded specimens of about 1 in. dia. x 1 in. heights were readily heated to about 3000°K with a 5-turn coil surrounding the current-concentrator previously described. Such heating of both pyrolytic and conventional graphite was accompanied by only modest pressure rises in the vicinity of the carbon specimen. An ion gauge placed just opposite the current-concentrator registered about 5×10^{-7} torr before heating. During heating to 2900°K to 3000°K over 10 to 30 min., pressures were kept below about 1.5×10^{-6} torr. The chief problem with this arrangement was the occurrence of periodic pressure bursts, presumably associated with arcing across the RF leads inside the feedthrough. These bursts were simulataneous with electrical surges which tripped off the RF generator and in severe cases, opened up leaks around the RF feedthrough gaskets.

c. The third arrangement chosen for testing was to simply eliminate the current concentrator and heat the carbon samples directly with small diameter work coils. Figure 8 shows a typical setup employing a self-shielded, pyrolytic graphite Knudsen cell. The output of the RF generator was connected directly to the RF feedthrough and several shielded and unshielded Knudsen cell arrangements were tested. These included an

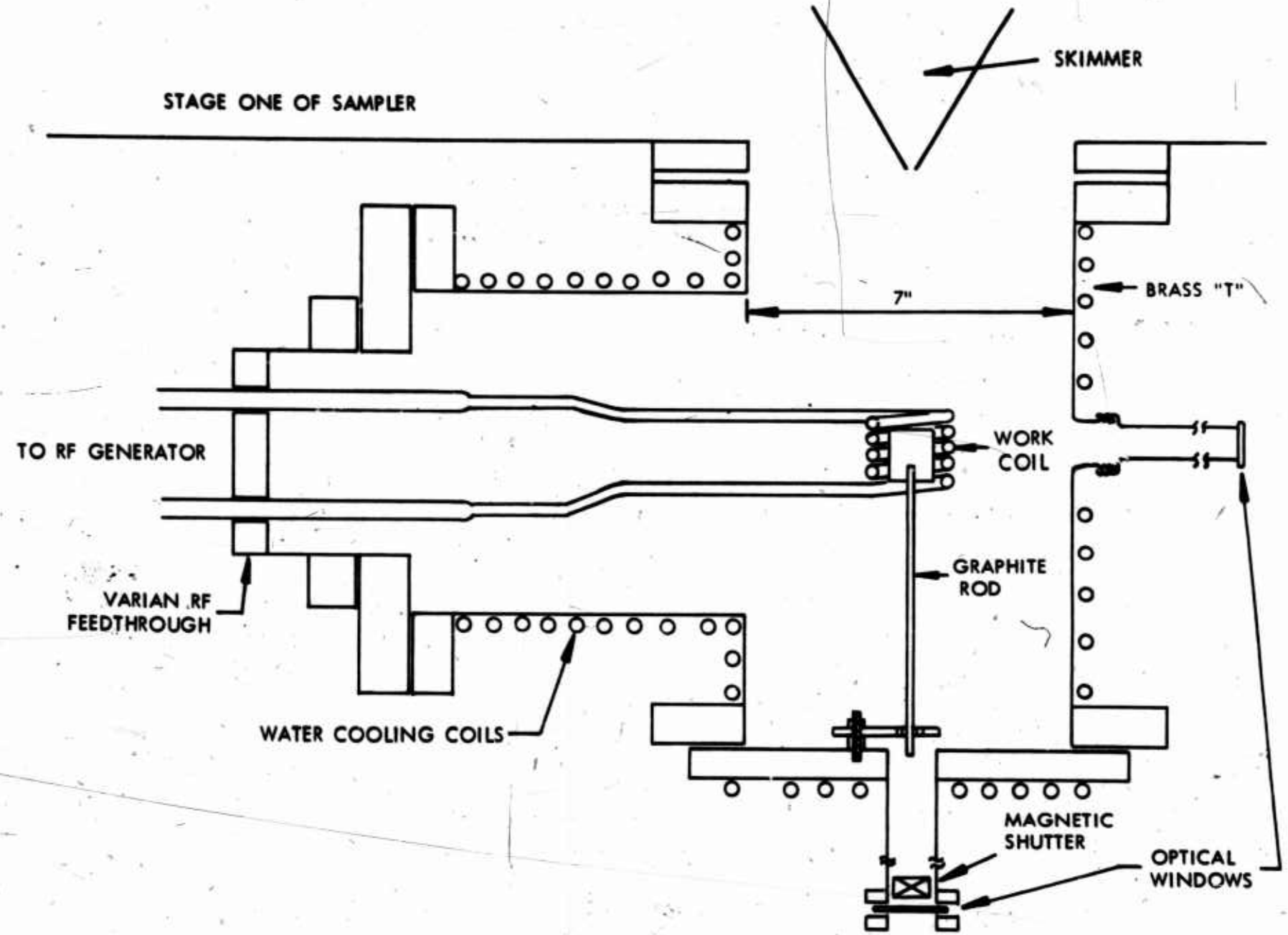

Figure 8 - Schematic of the Water-Cooled Housing in Which Direct RF Heating of Graphite Knudsen Cells in Vacuum Takes Place

ATJ Knudsen cell shielded with a split ATJ sleeve and a pyrolytic graphite Knudsen cell shielded with either an ATJ sleeve, with 0.001 in. Ta foil or left unshielded. In these various tests, temperature of the order of 2900°K to 3000°K were obtained but always, near the upper limits, pressure surges and arcing continued to terminate the heating.

d. The fourth arrangement represented an attempt to eliminate the arcing, the cause of which is still not definitely established. First, a 7:1 stepdown RF transformer was placed between the RF generator and the feedthrough so that substantially lower voltages would exist inside the vacuum system. Second, quartz shields were placed over the work-coil leads inside the vacuum, to shield the feedthrough ceramic from carbon vapor. Heating tests in air indicated that optimum coupling was achieved around a 1 in. x 1 in. graphite rod, for a 1-5/8 in. I.D. coil formed from 1/4 in. copper tubing, if three to five turns were used, spaced over a length of about 1-1/2 in.

A 1-1/2 in. I.D. four-turn coil of length 1-1/2 in. was chosen for the first vacuum tests of the transformer coupled heating of pyrolytic graphite cells. The first tests were with slotted PG cylinders, capped with slotted PG end pieces. A scale drawing of the cell and support arrangement is shown in Figure 9. With this arrangement, heating to 3000°K was accomplished, but again, arcing caused the RF generator to trip off. It will be prime priority to determine the reason for this arcing and to eliminate it so that temperatures of interest can be reached.

With the cell shown in Figure 9, beam measurements were made at several temperatures. A C_3^+ signal could readily be detected, at 17.0 ev, with cell temperatures of about 2320°K. At 2800°K, the cell was easily aligned within the rather large skimmer and the ions C_1^+, C_2^+, C_3^+, C_4^+, and C_5^+, C_6^+, C_7^+ were observed by phase-sensitive detection, at levels well above any background modulation effects (with the exception of C_7^+). Figure 10 gives the uncorrected relative ion intensities of the observed species from two experiments at the approximate temperatures of 2800°K and 2630°K. Also shown are the species ratios from Drowart et al. (Ref. 3). We adopt the same plotting scheme as Ref. 3, normalizing our uncorrected ion ratio results to C_1 pressures. The agreement is reasonable and the absolute beam intensities are consistent with the permanent gas beam calibrations mentioned earlier. Although some contribution from surface evaporation may be present in this loosely collimated system the results indicated that equilibrium is dominating, as judged from the C_3/C_1 ratios. These beam results indicate that as temperatures of 2800°K are exceeded, we should be able to detect several carbon species beyond C_5 in equilibrium with graphite.

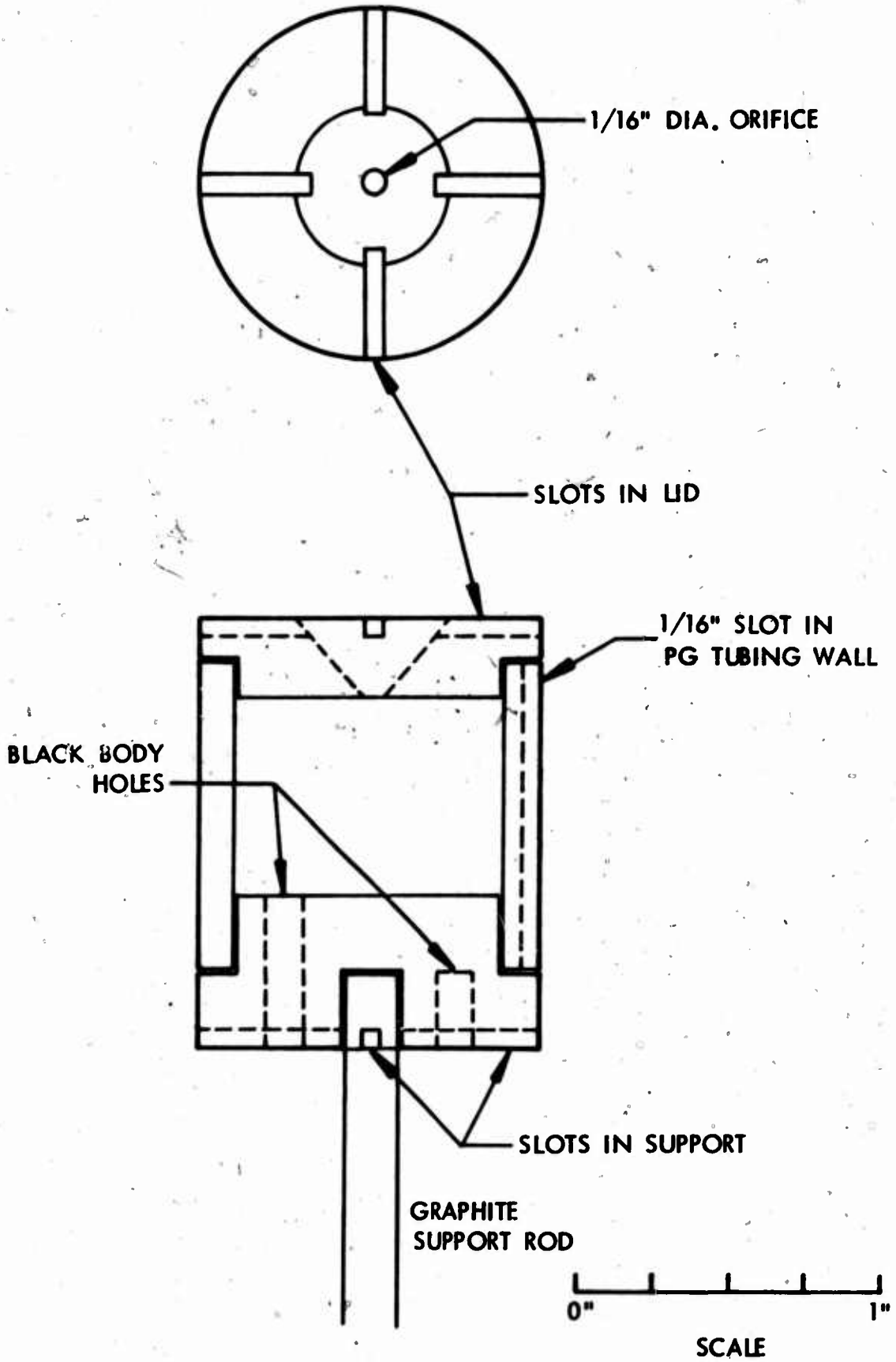

Figure 9 - Schematic of the Pyrolytic Graphite Knudsen Cell Used in Initial Heatings and Carbon Species Detection. A 7 to 1 step-down transformer was used.

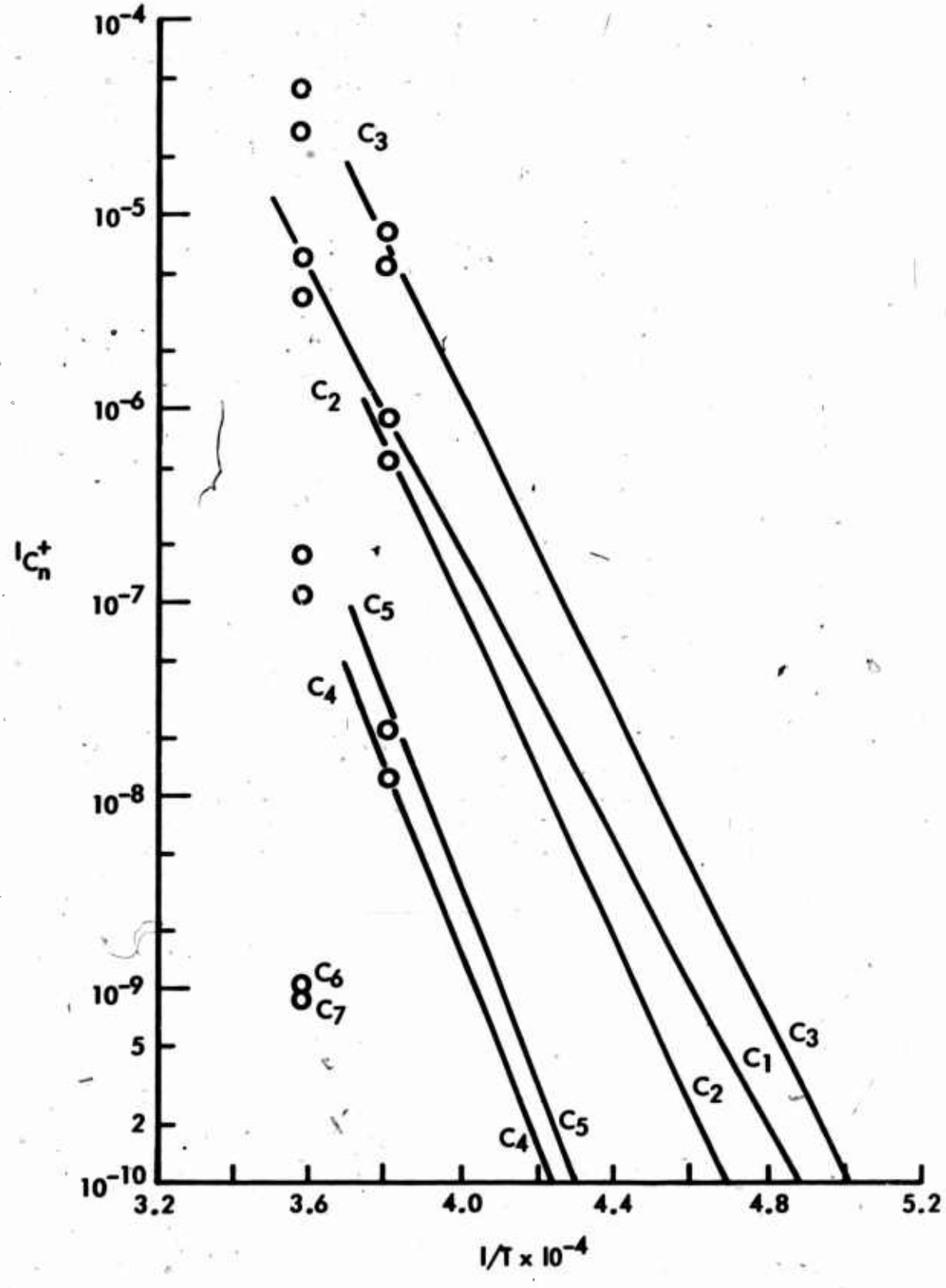

Figure 10 - Plot of Ion Intensity Ratios 1/T for Species Emerging from the Pyrolytic Graphite Knudsen Cell Shown in Figure 8. The data are normalized to C_1 in the manner used by Ref. 3.

C. Equilibrium Carbon Vapor Source Design

Two approaches to achieving equilibrium carbon vapor come readily to mind. One is to saturate a carrier gas with carbon vapor species in equilibrium with solid graphite and then sample mass spectrometrically the gas mixture. This conceptually simple transpiration experiment faces major problems in implementation in terms of cold-orifice sampling perturbation and condensation during beam formation. The carrier gas, at a given pressure of carbon vapor, will accelerate the free jet expansion cooling, and by providing a plentiful third-body, will enhance condensation kinetics. Nevertheless this scheme, which allows graphite to be its own container and permits high temperatures with minimum mass transport of carbon, has the greatest projected potentiality in the 1 atm. carbon pressure regime.

The second approach envisions a conventional Knudsen cell, with saturation achieved inside through large surface area to orifice area ratios. As pressures inside rise, one is again faced with sampling perturbations but in this case no cold probes are required and no permanent gas is present to enhance undesirable effects. The difficulty, of course, is that no suitable construction material for such a Knudsen cell exists except graphite itself. The problem then becomes one of distinguishing vapor that emerges from inside the cell, through the orifice, from that which evaporates freely from the surface surrounding the orifice. Under effusive flow conditions, a highly collimated detector, such as we can achieve with our molecular beam system, can be aligned to "see" only the inside of the cell. However, as soon as pressures increase to the point that gas-phase collisions are probable as the vapor leaves the orifice or surface, then the surface evaporated graphite can interact with and thus disturb in an unknown way the composition of the vapor leaving the orifice from inside the cell. This problem initially discouraged us from giving high priority to extended pressure range, graphite Knudsen cell studies. A further problem in vacuum heating of graphite Knudsen cells is that transport of graphite to colder surrounding objects becomes extreme as temperatures exceed 3000°K and in fact, the heat requirements to vaporize the material begin to be competitive with radiation losses at about 3400°K (see Ref. 7).

Discovery of a 1962 paper entitled "An Induction Furnace for Operations up to 3400°C Using Well Oriented Graphite" (Ref 14) has renewed our interest in the Knudsen cell approach. In this work it was established that extremely large temperature gradients could be established across very thin cylindrical walls of induction heated pyrolytic graphite ("well oriented graphite"). Furthermore, the emissivity of the basal plane of pyrolytic graphite (PG) was found to be about 0.6 in the 2000°C to 2500°C range, significantly reducing radiation heat losses. The simple scheme, shown in Figure 11a, which takes advantage of the very large anisotropy

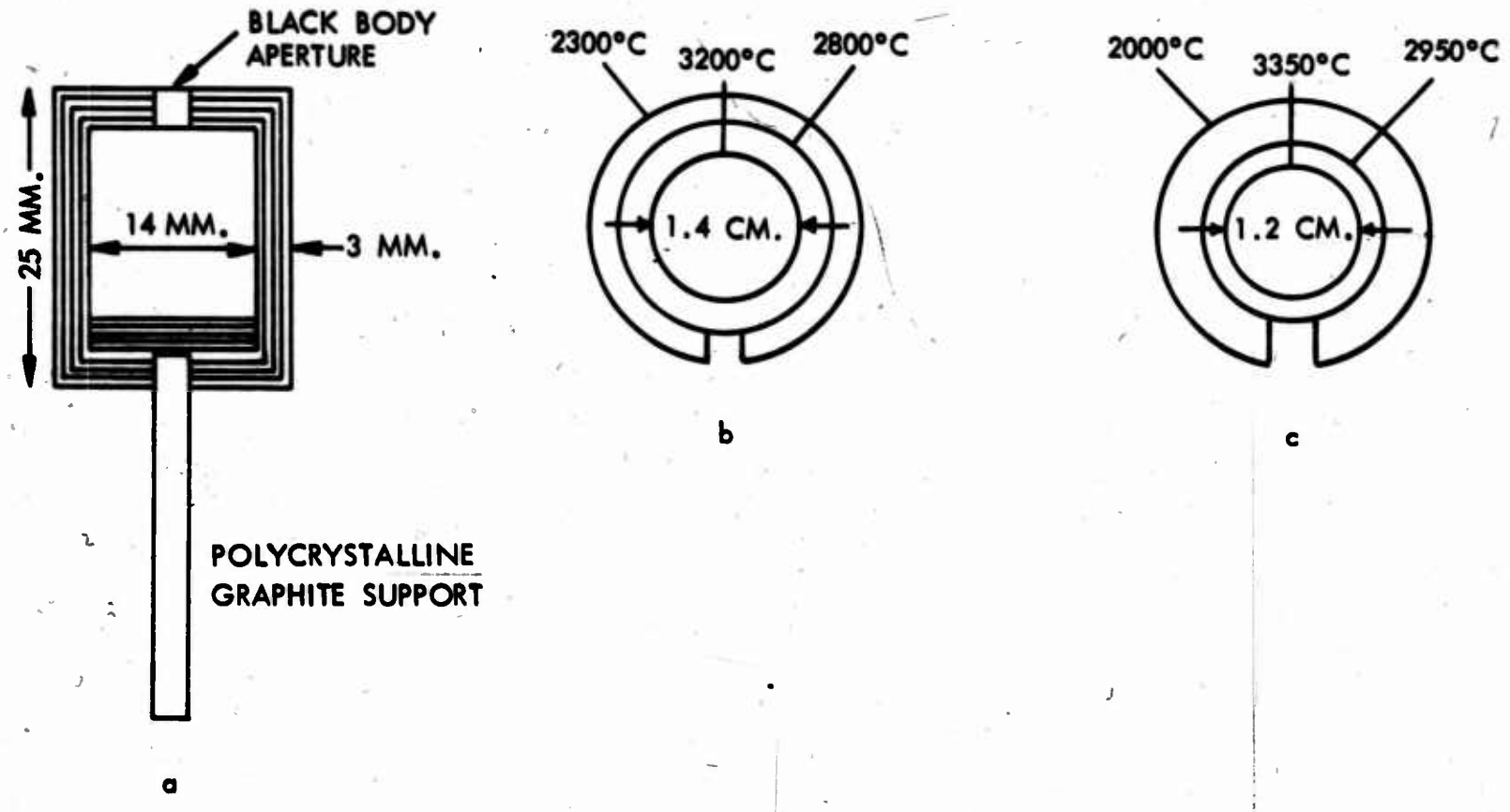

Figure 11 - Schematic of the Kinds of Pyrolytic Graphite Cells Tested in Ref. 14 and Typical Gradients Achieved Across Slotted Walls. Figure 11a shows the orientation of basal planes of the PG. Figure 11b had a slotted shield 1.5 mm. thick while Figure 11c had a susceptor thickness of 1.5 mm. and a slotted shield 3.5 mm. thick.

in thermal conductivity between the a and c plans of PG, was tested by Moore et al. (Ref. 14) in inert gases and vacuum. They heated closed-ended PG cylinders with a 25 kw., 500 kHz generator using direct coupling to water cooled, several-turn, copper work coils. The PG shield and susceptor were fabricated from the same integral piece of PG cylinder by simply cutting slots partially into the wall, the entire length of the cylinder. The kinds of gradients established in typical heatings in He gas at 1.5 atm. are indicated in Figures 11b and 11c (adapted from Ref. 14). It can be appreciated, from the enormous gradients produced, that PG provides a potential means of achieving equilibrium graphite vapor at quite high temperatures, with the evaporation of graphite and radiant heat losses greatly reduced. In fact behavior such as is shown in 11c, if it could be achieved with a Knudsen cell configuration such that interior vapor could escape undisturbed, would be nearly ideal for vacuum studies. If all external portions of the cell, with the exception of the slot and the immediate vicinity of the orifice, could be kept at temperatures below even 2400°C, then only the continuum expansion effects through the orifice would be of concern. In practice,problems can be expected in the slot and in the tapered region around the orifice. Figure 12 shows the cell used for the beam studies reported above. The difference in color in the lid and cylinder show graphically the anisotropic properties of PG. Note especially the effect of slotting on the induction heating of the cylinder.

The cell design shown in Figure 13 will be tested next to improve heating behavior in vacuum and to try to circumvent the limitations mentioned above. A baffle will be inserted to block line of sight between the two orifices. Outer slotted tubing with wall thickness 3/16 in. will be used. In Ref. 14 it was only indicated that operation in vacuum to above 2600°C could be readily carried out. It is hoped ultimately that Knudsen cell equilibrium vapor can be observed at temperatures to 3600°K with such an arrangement, and that an assessment of the conditions for onset of continuum expansion can be made. As pointed out in Ref. 14, PG tubes also make valuable resistor furnace elements. For example, it was reported that a 13 mm. I.D. tube, with 4 mm. walls, could be resistively heated to around 3600°C inside temperature while the surface temperature was only 2250°C. Such tubes thus recommend themselves for the transpiration type experiments which are probably necessitated at carbon pressures approaching anything like 1 atm.

D. Continuum Effects

Pending the results of the studies of graphite vaporization at high pressures, we have continued to speculate about the conditions under which continuum expansion of carbon vapor might lead to a perturbation of the gaseous composition leaving the surface. This speculation has been heightened by three recent inputs. First, we have collected all our past observations on the dimerization of pure gases during free-jet expansion.

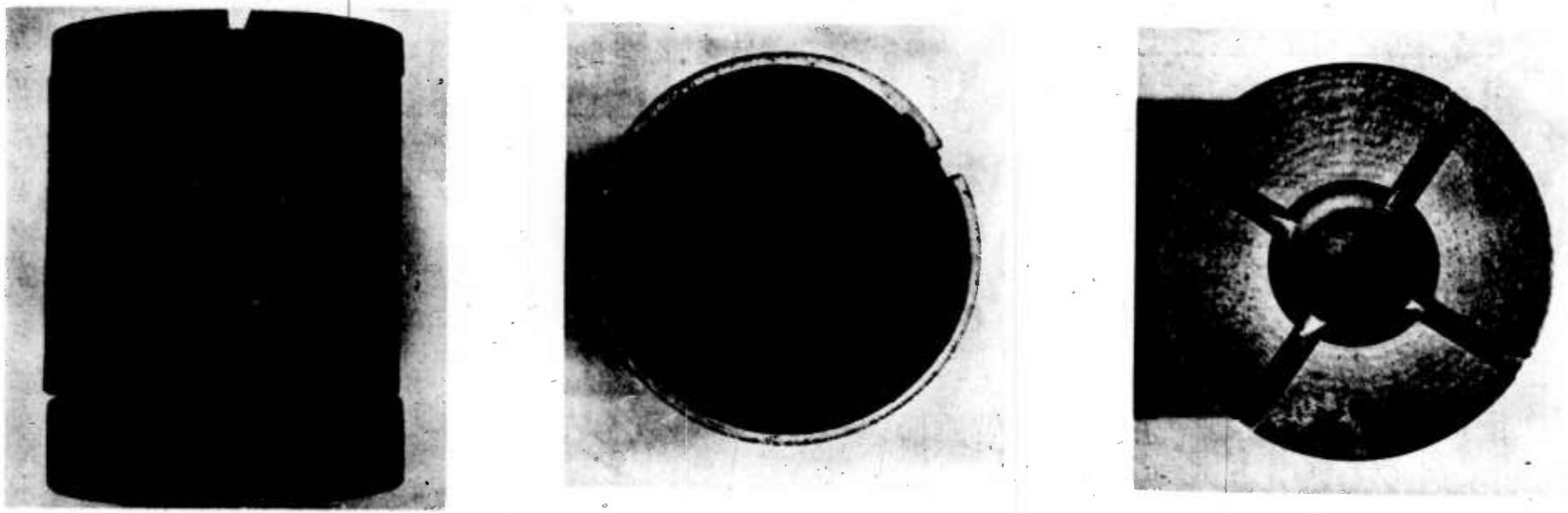

Figure 12 - Photographs of the Pyrolytic Graphite Cell Used in the 2800°K Heating for Which Data are Shown in Figure 10. In Figure 12a note the sharp temperature gradient in the lower lid due to the slot. Also the delamination and shifting of lamella along the slotted cylinder. In Figure 12b note the sharp color gradient and delamination around the cylinder at the slot depth (originally slotted halfway through). Also note the extensive delamination of the inner, unslotted portion of the cylinder. In Figure 12c note the gradients along the rather thick conical, slotted orifice-lid.

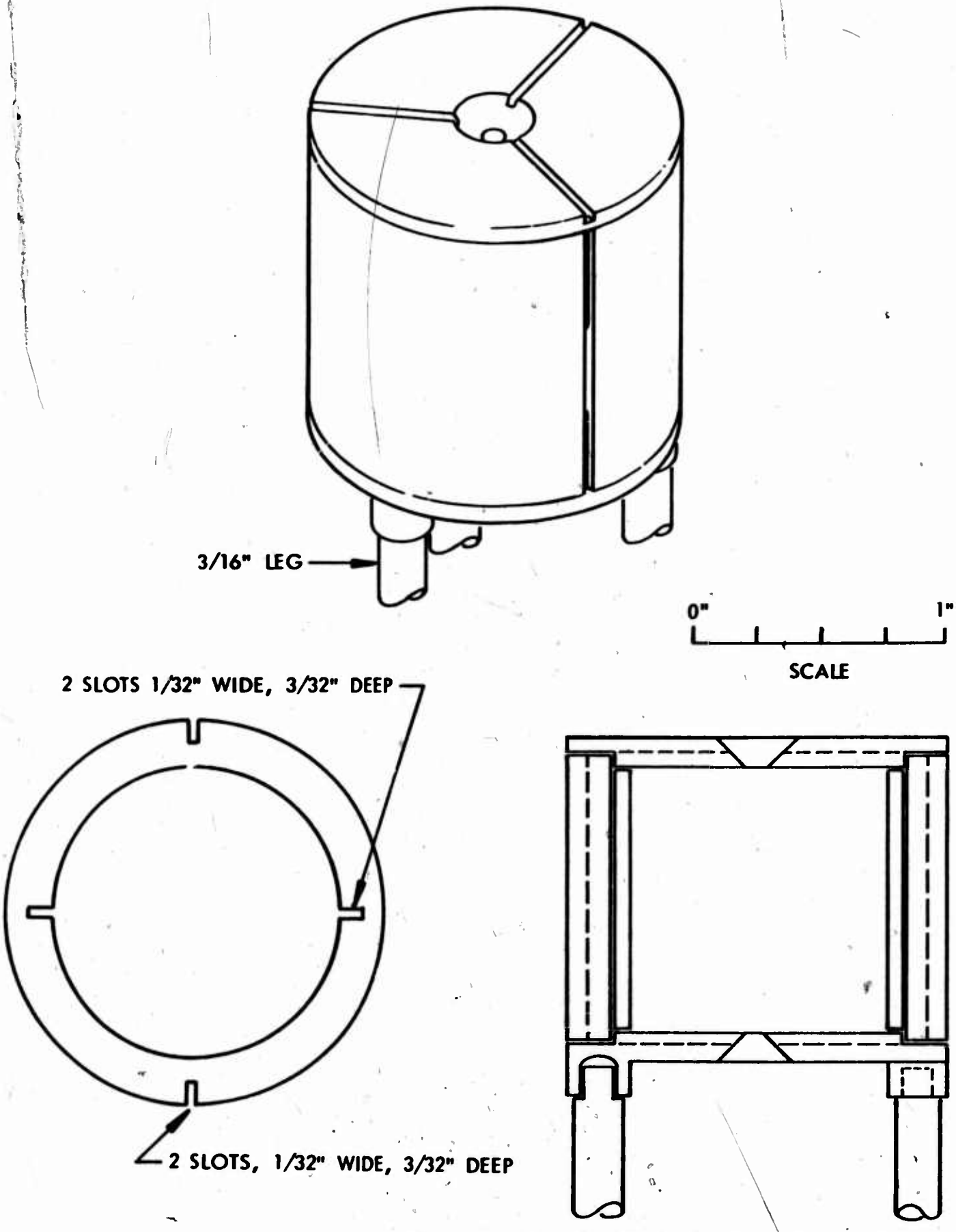

Figure 13 - Schematic of the Pyrolytic Graphite Knudsen Cell Design to be Tested for Minimizing Vapor and Radiation Losses and Arcing. The inner cylinder is unslotted 1/16 in. wall PG tubing.

Following our successful treatment of argon dimerization (Ref. 15), we attempted to correlate the excess mole fraction of dimer with the parameter $P_o^2 d$, where P_o is the source pressure and d is the orifice diameter. Such a correlation, without regard to source temperature, is shown in Figure 14. The outstanding feature of these correlations is the enormous range of variation with different substances and with temperature. Thus H_2O appears to nucleate some three orders of magnitude more readily than Ar. Temperature effects seem to be present as judged from the water data. At present, we have no basis to predict the effects of temperature, bond energy, molecular structure, and specific heat ratio on the source conditions at which nucleation will become important. Particularly for strongly bound metals and graphite is the range of possibilities open, so that only direct experiment with the substance of interest is likely to provide an answer.

Another input concerns recently reported experiments in which nucleation may well occur but is not explicitly discussed or eliminated. Nucleation may be of marginal importance in measurements of very small amounts of equilibrium dimer such as Kant and co-workers have recently reported. For example, Kant and Lin (Ref. 16) report a dimer-to-monomer ion-ratio for Ti of only 2.6×10^{-6} over Ti metal at 2337°K. If one assumes a vapor pressure of Ti of about 4×10^{-4} atm., then expansion through an orifice of 1 mm. dia. gives a $P_o^2 d$ equal to 3.6×10^{-4} torr^2 in. It is not impossible to believe, from extension of behavior shown in Figure 11, that some nucleation may be contributing to the dimer mole fraction observed in such experiments.

A third and much more intriguing case is that of laser evaporation, during which very high source pressures and temperatures are presumably achieved. For example, Ban and Knox (Ref. 17) recently presented data on the vaporization of antimony and tellurium heated to temperatures and pressures presumed to be in the vicinity of the critical point. They speculate about the nature of the various mass spectrometrically observed species in terms of the species and of the short-range order present at critical conditions, although they do not discuss the possibility that nucleation processes alter the composition during the plume expansion. In a later paper an experiment is described (Ref. 18) to assess the importance of plume reactions, but the results appear ambiguous to us. Even if they obtained plume diameters as small as 0.0001 in. (0.0005 in. dia. craters have been reported), the 10^3 atm. pressure postulated would still result in $P_o^2 d$ of about 6×10^7! It is thus very hard to believe that beam formation can occur under such conditions without substantially altering the gaseous composition. All of this discussion points to the desirability of obtaining some measurement of typical onset of nucleation phenomena in metals and carbon at high temperature.

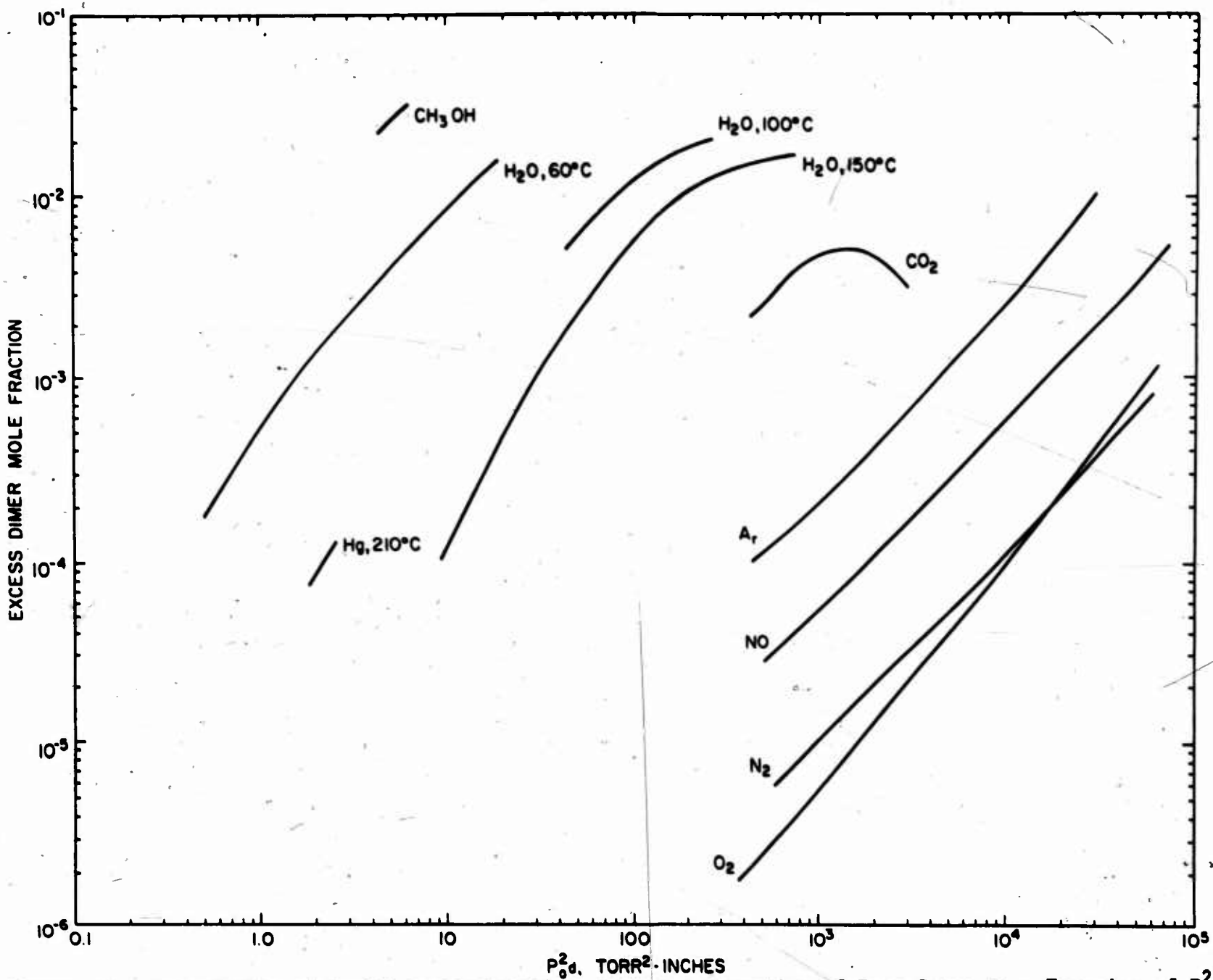

Figure 14 - Correlation of Excess Dimer Formed in Free-Jet Expansion of Pure Gases as a Function of P_o^2d, the Source Pressure Squared Times the Orifice Diameter

IV.

WORK PLANNED FOR THIRD YEAR

The third year will be devoted to achieving two principal goals: (1) Observing the equilibrium composition of carbon vapor in the temperature range of 3000°K to 3600°K (total pressure approaching 10^{-1} atm.) from PG Knudsen cells, and (2) Assessing the conditions for onset of composition perturbations due to the continuum expansion effects of mass separation and nucleation. Important developmental tasks to achieve these goals will be: (1) the fabrication of PG Knudsen cells to achieve interior temperatures up to 3600°K while allowing relatively undisturbed escape of the vapor, and (2) to implement the time-of-flight, pulse-counting, rapid data acquisition system presently assembled to permit both composition and velocity measurements to be carried out on pairs of species in times of the order of seconds (before cell deterioration occurs).

APPENDIX

ELECTRONIC AND MECHANICAL COMPONENTS OF MODULATED-BEAM PRODUCTION AND DETECTION SYSTEM

Chopping System

Photocell - Centralab Electronics Division, Type IN 2175
Lamp - Chicago Miniature Lamp Works, CM8-680
Audio Oscillator - Hewlett Packard, 200 AB
Power Amplifier - Heathkit Stereo Amplifier, AA-14 (Modified)
Motor - Globe Industries, Model 53A477 or 53A116-2, Type SC

Analog Detection

Phase Sensitive Detector - Princeton Applied Research JB-4
Electrometer Amplifier - Nuclide Model EA-4

Ion Counting Detection

NIM Power Supply - Hewlett Packard, Model 5580B
Preamp/Amplifier - Hewlett Packard, Model 5554A
Linear Amplifier - Hewlett Packard, Model 5582A
Single Channel Analyzer - Hewlet Packard, Model 5583A
Multichannel Analyzer - Hewlett Packard, HO3-5401A
Pulse Generators - Systron-Donner, Model 100A

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13. ABSTRACT

The progress in a second year of study of the thermodynamics of carbon vapor is reviewed. The status and preliminary performance of a high capacity, three-stage, high pressure sampling system--Nuclide HT-12-90 mass spectrometer detector and data acquisition system (including time-of-flight velocity analysis of beam neutrals) is presented. Beam system calibrations with Ar, N_2 and Ag indicate partial pressures of about 1×10^{-10} to 1×10^{-8} atm. (depending on background) can be detected from a Knudsen cell with a 0.040 dia. orifice placed 56 cm. from the ion source. A troublesome feature of the present ion source is that some modulation of background peaks occur in the presence of modulated beams. A series of attempts to heat graphite in vacuum to temperatures greater than 3000°K are described. Best results are obtained with slotted pyrolytic graphite cells but arcing still limits heating to 3000° to 3100°K. Carbon species through C_7 have been observed from a pyrolytic graphite Knudsen cell. The C_1 to C_5 data agree well with literature values, at the two temperatures of 2800°K and 2630°K. A correlation of dimer formation versus expansion conditions for a number of gases studied to date, indicates that nucleation cannot be ruled out in high-pressure Knudsen cells or laser heatings.

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